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THE THERMAL AND PHOTOCHEMICAL REACTIONS OF 3H-1, 2-DIAZEPINES
A NEW VARIATION ON THE DIAZEPINE-PYRAZOLE REARRANGEMENT

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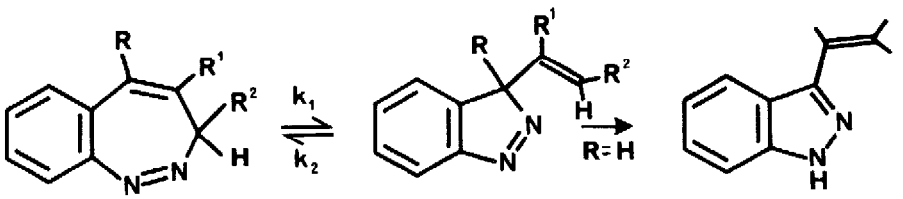
We have recently reported two variations of the new rearrangement between 3H-1, 2-benzodiazepines and pyrazoles which formally involves a 1, 3-shift of the azo-group. Benzodiazepines of type (1a), with no hydrogen atom attached to the migration terminus, undergo both heat and light induced reversible interconversion with 3-vinylindazoles (2a).[1] In the thermal reaction at 130°C in hexadecane the equilibrium favours the indazole (k_1/k_2 = 2.0) for (1a, R = Ph). It has also been shown that similar 1, 2-benzodiazepines (1b) which do have hydrogen attached to the 5-position undergo irreversible photochemical ring contraction to give 1H-indazoles[2] (3), presumably via (2, R = H) which aromatises by a proton shift.



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a, R = Ar, R^1R^2 = $-(CH_2)_3-$
b; R = H

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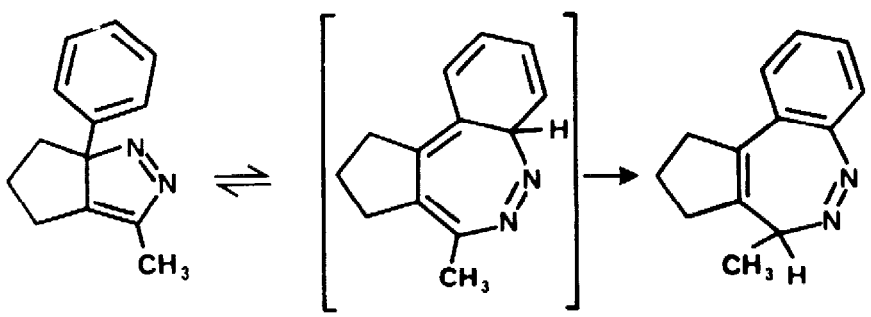
Another variant of this rearrangement, irreversible in the opposite direction, is the thermal ring expansion of the 3H-pyrazoles (4) to the benzodiazepines (5).[3]



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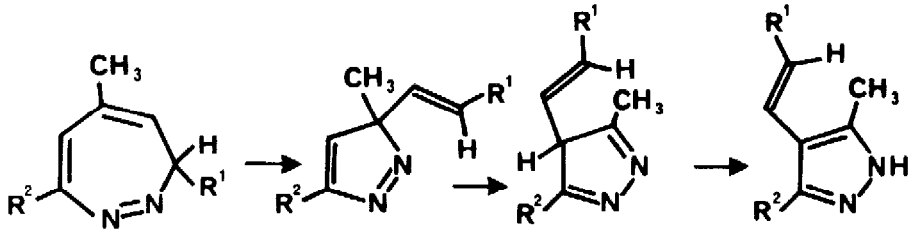
Again it appears that the primary rearrangement product is converted to a more stable isomer by a facile hydrogen migration, so driving the reaction to the right.

In view of these reactions it was of interest to examine the rearrangement potential of the recently synthesised 3H-1, 2-diazepines[4] (6) and it was found that the thermal and photochemical reactions take quite different paths. When heated at 110°-130° the diazepines (6a, b) contracted to the 1H-pyrazoles (8) apparently by three consecutive rearrangements



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a, $R^1 = R^2 = CH_3$

b, $R^1 = H$, $R^2 = CH_3$

7

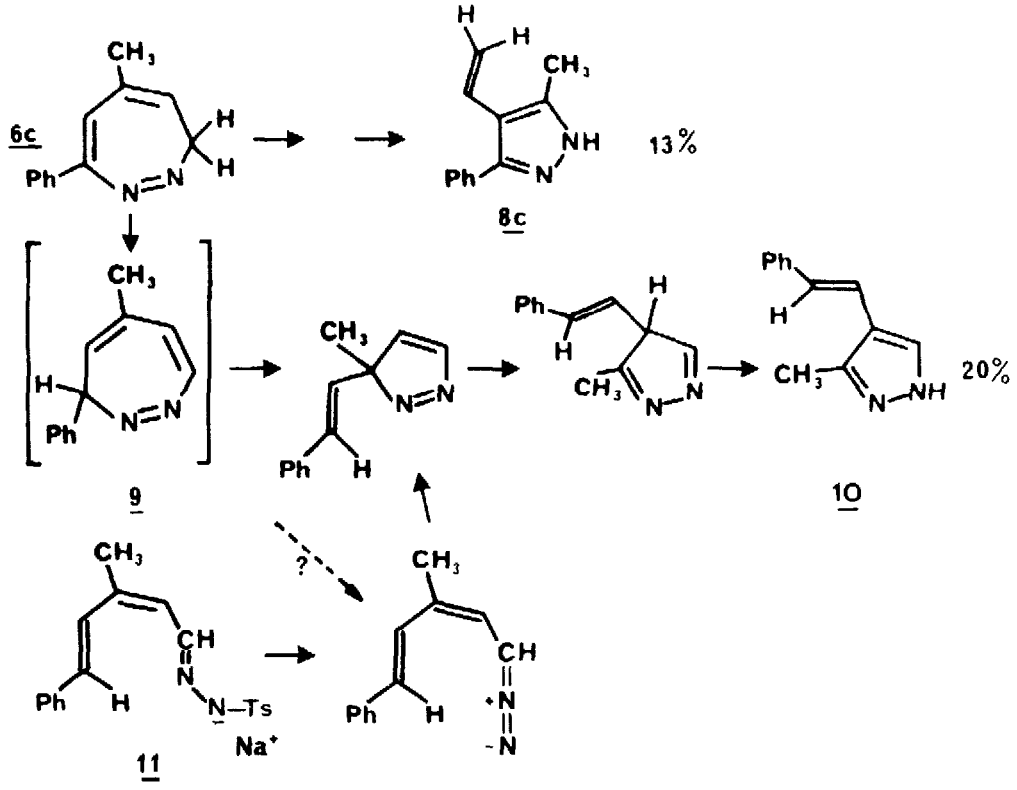
8 (a) 53%

(b) 40%

The initial ring contraction parallels the (1) to (2) conversion above and is followed by a [1, 5] migration of the vinyl group and then by a hydrogen shift The second step is the first report of the shift of a vinyl group in a thermal van Alphen-Huttel rearrangement That the vinyl group migrates in preference to the methyl group is consistent with earlier reports of the relatively high mobility of vinyl groups in sigmatropic shifts The last step reflects the well known instability of 4-hydro-4H-pyrazoles relative to the aromatic 1H-isomers In the rearrangement of intermediate (7), as in the thermal rearrangement of other 3H-pyrazoles,[3] direct [1, 5] group migration from the saturated carbon to the adjacent nitrogen does not occur, the alternative [1, 5] shift to carbon always seems to be preferred Since the overall free energy change for the notional C to N shift, which would give an aromatic pyrazole directly, would doubtless be greater than that for the observed C to C shift which gives the non-aromatic 4H-pyrazole, the preference for the latter must be due to kinetic factors, probably relating to more favourable orbital overlap in the transition state

The rearrangement of the diazepine (6c) is more complex and gives two pyrazoles (8c) and (10). The former is derived in the usual way but the genesis of the latter most probably involves a [1, 5] hydrogen shift in the diazepine, giving (9), which precedes ring contraction and vinyl migration Attempts to synthesise (9) or to detect it during the course of the pyrolysis have so far been unsuccessful but we have shown that (10) is also found (16%) in the decomposition of the tosylhydrazone salt (11)

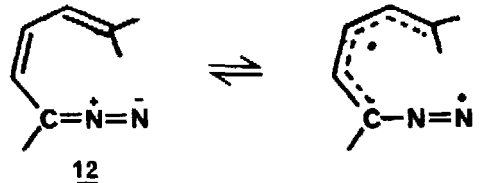
All the rearrangement reactions are accompanied by loss of nitrogen from the diazepines to give hydrocarbons, e g methylphenylcyclopentadiene and its dimer were



detected by mass spectrometry in the products from (6c), and hydrogenation of the hydrocarbon fraction gave 1-methyl-3-phenylcyclopentane (19%) The latter was also similarly obtained from the decomposition of (11)

All the pyrazole products were characterised by their spectra and analysis and by comparison of the properties of their hydrogenated derivatives with literature data or samples prepared by alternative routes

It seems most likely that the general ring interconversion between diazepines and pyrazoles proceeds stepwise via intermediates like (12) which can be written as dipoles or diradicals, and that the nature of the final product depends on steric factors and on the capacity of the pyrazole or diazepine to convert irreversibly to a stable isomer



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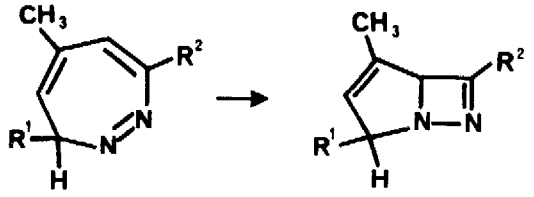
The intermediacy of diazo-compounds supported by the formation of (10) from (11) and by trapping experiments with tributylphosphine which will be discussed in the full report

Unlike the photoisomerisations of (1a) to (2) and (1b) to (3) the light induced reactions of (6) take a different path and parallel the reactions of 1H-2, 3-benzodiazepines[5] in giving the [1, 2] diazeto [4, 1-a]pyrroles (13) in high yield.



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